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3,835,000

ELECTROLYTIC PROCESS FOR PRODUCING N-PHOSPHONOMETHYL GLYCINE

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19 Claims

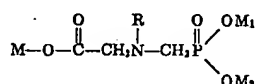
ABSTRACT OF THE DISCLOSURE

This disclosure relates to an electrolytic process for producing N-phosphonomethyl glycine compounds by the electrolysis of N-organo-N-phosphonomethylamino acetic acid compounds. In accordance with this disclosure, a solution of an N-organo-N-phosphonomethylamino acetic acid compound is subjected to an electromotive force or electric current in an electrolytic cell to be electrolytically oxidized to an N-phosphonomethyl glycine. The N-phosphonomethyl glycines produced are useful as post-emergent herbicides.

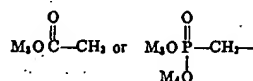
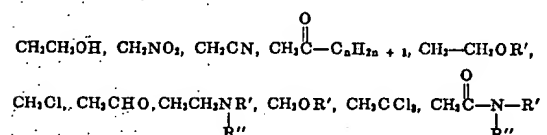
This application is a continuation-in-part of application Ser. No. 317,498, filed Dec. 21, 1972.

This invention relates to a method of producing N-phosphonomethyl glycines by the electrolytic oxidation of N-organo-N-phosphonomethylamino acetic acid compounds. More particularly, this invention relates to the production of N-phosphonomethyl glycines by the electrolysis of N-organo-N-phosphonomethylamino acetic acid in an aqueous medium.

In accordance with the process of this invention, an aqueous electrolytic solution or suspension of an N-organo-N-phosphonomethylamino acetic acid compound of the formula



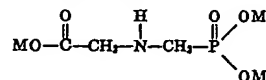
wherein R is a member of the class consisting of allyl, halogen-substituted allyl, benzyl, halosubstituted benzyl, 2,2,2-triphenylethyl, diphenylmethyl, 1,2- or 2,2-diphenylethyl,



groups wherein R' is alkyl of from 1 to 6 carbon atoms, R'' is hydrogen or R' and M, M₁, M₂, M₃ and M₄ are each individually hydrogen, alkoxyalkyl groups, alkyl groups of from 1 to 18 carbon atoms, preferably lower alkyl, alkali metal, alkaline earth metal, ammonium and organic ammonium, provided that at least one of M, M₁ or M₂ is H, alkali metal or alkaline earth metal and n is an integer of 1 to 6 is charged into an electrolytic cell fitted with an anode and a cathode and an electromotive force or electric current impressed upon the cell whereby the N-organo-N-phosphonomethylamino acetic

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acid is electrolytically oxidized to yield an N-phosphonomethyl glycine of the formula



wherein M, M₁, and M₂ are as above defined as the principal product.

The alkoxyalkyl groups represented by M, M₁, M₂, and M₄ include

methoxyethyl,
4-ethoxy-2-methylbutyl,
2-ethoxyethyl,
3-methoxypropyl,
4-methoxybutyl,
4-methoxy-2-ethylbutyl,
4-butoxybutyl,
2-(2-methoxyethoxy)ethyl,
2-(2-butoxyethoxy)-ethyl

and the like.

The alkyl groups represented by R', M, M₁, M₂, M₃ and M₄ include lower alkyls such as methyl, ethyl, propyl, isopropyl, butyl, pentyl and hexyl, as well as the higher alkyls such as heptyl, octyl, dodecyl, octadecyl and the like.

The term "alkali metal" encompasses lithium, sodium, potassium, cesium and rubidium; and the term "alkaline earth metal" includes beryllium, magnesium, calcium, strontium and barium.

The organic ammonium groups represented by M, M₁, M₂, M₃ and M₄ are those derived from lower molecular weight organic amines, i.e., those having a molecular weight below about 300. Such organic amines include the alkyl amines, alkylene amines and alkanol amines containing not more than 2 amine groups, such as methylamine, ethylamine, n-propylamine, isopropylamine, n-butylamine, isobutylamine, sec-butylamine, n-amylamine, isoamylamine, hexylamine, heptylamine, octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, methylethylamine, methylisopropylamine, methylhexylamine, methylnonylamine, methylpentadecylamine, methyloctadecylamine, ethylbutylamine, ethylheptylamine, ethyloctylamine, hexylheptylamine, hexyloctylamine, dimethylamine, diethylamine, di-n-propylamine, diisopropylamine, di-n-amylamine, diisoamylamine, dihexylamine, diheptylamine, dioctylamine, trimethylamine, triethylamine, tri-n-propylamine, triisopropylamine, tri-n-butylamine, triisobutylamine, tri-sec-butylamine, tri-n-amylamine, ethanamine, n-propanamine, isopropanamine, diethanamine, N,N-diethylethanamine, N-ethylpropanamine, N-butylethanamine, allylamine, n-butenyl-2-amine, n-pentyl-2-amine, 2,3-dimethylbutenyl-2-amine, di-butenyl-2-amine, n-hexenyl-2-amine and propylenediamine, primary aryl amines such as aniline, methoxyaniline, ethoxyaniline, o,m,p-toluidine, phenylenediamine, 2,4,6-tribromoaniline, benzidine, naphthylamine, o,m,p-chloroaniline, and the like; heterocyclic amines such as pyridine, morpholine, piperidine, pyrrolidine, indoline, azepine and the like.

In a preferred method of conducting the process of this invention, a 2% to 30% solution of the N-organo-N-phosphonomethylamino acetic acid compound dissolved in 1.0% to 37% hydrochloric acid (1-37% HCl in water) and even more preferred, 10-25% HCl, is charged into an electrolytic cell maintained at a temperature of from 25° C. to 110° C. and having noble metal, graphite or carbon electrodes. An electric current is then impressed on the cell by connecting the anode and cathode

to a proper source of direct current with controls to maintain the current density at between 1 and 700 ma./cm.² for a time sufficient to oxidize the N-organo-N-phosphonomethylamino acetic acid compound to the N-phosphonomethyl glycine.

The resultant reaction solution is then vacuum evaporated to remove the aqueous hydrochloric acid reaction medium and volatile by-products. The residue is then dissolved in water and recovered by recrystallization upon the cooling of the water solution.

The concentration of the N-organo-N-phosphonomethylamino acetic acid compound employed in the process of this invention is not critical and is limited only by the solubility of the starting material in water. Thus, for example, although concentrations as low as 0.01% by weight in water can be employed, for reasons of efficiency and economy, it is preferred to employ concentrations of from about 5 to about 30% by weight, or even higher, of the N-phosphonomethylamino acetic acid compound in an aqueous electrolyte.

The temperature at which the process of the instant invention is conducted is not narrowly critical and can range from as low as 0° C. to as high as 110° C. or even higher if a pressure cell is employed. As is apparent to those skilled in the art, at lower temperature a very dilute solution or a suspension must be employed since the solubility of the N-organo-N-phosphonomethylamino acetic acid starting material is lower at lower temperatures.

The process of the instant invention can be conducted at atmospheric pressure, super atmospheric pressures and subatmospheric pressures. For reason of economy and ease of construction of the equipment employed in the process of this invention, it is preferred to conduct this process at approximately atmospheric pressure.

The type of electrolytic cell employed in the process of this invention is not critical. The cell can consist of a glass container having one or more anodes and cathodes connected to a source of direct current, such as a battery and the like or a source of low frequency alternating current. The cell can also consist of the two electrodes separated by an insulator such as a rubber or other non-conducting gasket.

The current densities employed in the process of this invention can range from as low as 1 milliamperes per square centimeter (ma./cm.²) to 700 or more ma./cm.².

The electrodes, i.e., the anode and cathode, employed in the process of this invention can be constructed of a wide variety of materials and combinations of materials. Thus, for example, the anodes may be constructed of any conductive substance, such as lead, graphite, lead oxide, lead sulfate, carbon in various forms, platinum, various metal oxides such as manganese dioxide, copper oxide, nickel oxide and the like, and can be in many different forms such as gauze, solids, porous, etc.

The cathodes can also be of any conductive substance such as copper, lead, platinum, palladium, lead oxide, graphite, carbon and the like. It is preferred to employ a noble metal such as palladium or platinum or various forms of graphite, carbon or glassy carbon as the electrode materials employed in the process of this invention. Other electrode materials are less preferred since they corrode rapidly and their ions contaminate the electrolyte, thereby rendering the isolation of the product more expensive and difficult.

The acids which can be employed to render the aqueous medium acidic include the hydrohalic acids such as hydrochloric, hydroiodic, hydrobromic and hydrofluoric and other inorganic acids such as sulfuric, nitric, phosphoric, perchloric, tetrafluoroboric, trifluoroacetic and other strong organic acids such as toluene sulfonic acid, etc. and hexafluorophosphonic, etc.

For ease of removal, economy and convenience, it is preferred to employ aqueous hydrochloric acid as the aqueous medium in the process of this invention. The other acids can cause more difficult removal, corrosion and the like.

The bases which can be employed to render the aqueous medium basic include the alkali and alkaline earth metal oxides and hydroxides such as, for example, sodium, potassium, rubidium, cesium, calcium and barium, oxides and hydroxides, and organic bases such as tetraalkyl ammonium hydroxides, tertiary amines and the like.

It is, of course, apparent to those skilled in the art that the aqueous medium must be a conducting aqueous medium to obtain the best flow of current. Thus, the acids or bases or salts of such bases can be employed to make the electrolytic solution conductive.

It is, of course, apparent to those skilled in the art that the time of reaction is variable and is determined by variables such as current density, electrode area concentration and volume of the reaction solution.

In the process of the present invention, among the by-products produced is formaldehyde. The formaldehyde produced sometimes reacts with the product to produce N-methyl-N-phosphonomethyl glycine. It has been found that this secondary reaction can be eliminated or substantially suppressed by the employment of a formaldehyde scavenging agent such as urea, etc. However, for best results, it is preferred to control the parameters of the reaction, i.e., temperature, concentration and reaction time, to substantially eliminate the need for employing such agents inasmuch as they may interfere with the crystallization and recovery of the N-phosphonomethyl glycine product.

The N-phosphonomethyl glycine product of the process of the present invention is recovered from the reaction solution by conventional techniques known to those skilled in the art, such as by extraction and recrystallization, centrifugation, concentration and the like.

Thus, for example, the reaction solution can be vacuum evaporated to eliminate the water, acid, and volatile by-products. The solid which remains can be dissolved in water and then cooled to precipitate the N-phosphonomethyl glycine, which is recovered by filtration.

The product can also be recovered and purified by crystallization from a mixture of isopropanol and water.

The N-organo-N-phosphonomethylamino acetic acid compounds employed in the process of this invention can be produced by the reaction of the appropriate amine with formaldehyde and phosphorous acid in the presence of hydrochloric acid in accordance with the process set forth in U.S. Pat. 3,288,846.

The following examples serve to further illustrate this invention. In the examples, all parts are parts by weight unless otherwise expressly set forth.

EXAMPLE 1

To a suitable glass reaction vessel fitted with a graphite anode and a platinum cathode was added a solution consisting of N-phosphonomethylamino diacetic acid (15 g.), sodium hydroxide (4.6 g.) and water (60 ml.). The temperature of this reaction solution was about 16° C. and the pH was maintained at about 3 with a pH stat. The anode and cathode were connected to a potentiostat with the anode potential at 0.9 volts vs. SCE. The initial current was 112 milliamps dropping to 25 ma. after 64 hours. The reaction mixture was then analyzed by nuclear magnetic resonance spectral analysis and was found to contain 7.7% N-phosphonomethylamino diacetic acid; 72% N-phosphonomethylglycine and 15.4% N-methyl-N-phosphonomethyl glycine.

EXAMPLE 2

Into an electrolytic cell containing a graphite anode and a platinum cathode was charged N-phosphonomethylamino diacetic acid (15 g.) dissolved in 50 milliliters of concentrated hydrochloric acid. An electrical current giving a potential of about 1.09 volts vs. SCE was passed through the cell and solution for about 65 hours at about 10-15° C. until a total of 18,060 coulombs of electricity had been employed.

The reaction mixture was then analyzed by nuclear magnetic resonance spectral analysis and found to contain

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9.2% N-phosphonomethylimino diacetic acid; 7.5% N-phosphonomethyl glycine; 7.4% N-methyl-N-phosphonomethyl glycine and 6.1% N,N-dimethyliminomethylene phosphonic acid.

EXAMPLE 3

A sandwich cell composed of two graphite discs 4 1/4 inches in diameter separated by a U-shaped rubber gasket and clamped between two insulators with a C clamp and having a volume of about 25 ml. was employed. Into this cell was charged 20 ml. of concentrated hydrochloric acid containing N-phosphonomethylimino diacetic acid (4.5 g.), dissolved therein. It was necessary to heat the hydrochloric acid to dissolve the imino diacetic acid, however, it remained in solution on cooling. An electrolysis was carried out with the anode potential at 1.05 to 1.17 volts vs. SCE (initial current 300 ma.) for 4 hours and 40 minutes until 0.524 faradays of electricity had been passed.

The reaction solution was analyzed and found to contain N-phosphonomethyl glycine, some unreacted starting material and N,N-dimethyliminomethylene phosphonic acid and N-methyl-N-phosphonomethyl glycine.

EXAMPLE 4

N-Phosphonomethylimino diacetic acid (15 g.) dissolved in 50 ml. of concentrated hydrochloric acid was subjected to electrolytic oxidation in a glass cell employing graphite electrodes at 40° C. A constant current of 200 ma. was applied (anode potential of 2.1 volts vs. SCE) for approximately 26 hours, during which time the anode potential had decreased to 1.8 volts and the solution level in the cell had dropped about 10%.

The reaction solution was decanted into a flask, the cell and electrodes washed with approximately 100 ml. of concentrated hydrochloric acid and the washings combined with the reaction solution. The solution was then vacuum evaporated to yield 22.6 grams of a white solid. The white solid was assayed and found to contain 39.1% by weight of N-phosphonomethyl glycine, representing a 79.5% yield based upon the starting material.

EXAMPLE 5

A series of experiments were conducted employing a sandwich cell similar to that employed in Example 3, but employing electrolytically pure graphite and fitted with heating elements to maintain the temperature at 80° C.

In this experiment, the temperature was maintained constant at 80° C. and a constant current of 300 ma. applied for various times. When the current was applied for a total of 55 minutes, a yield of N-phosphonomethyl glycine in the range of from 80 to 90% based on starting N-phosphonomethylimino diacetic acid was obtained.

In a similar experiment wherein the current was applied to 18 ml. of 5% solution of N-phosphonomethylimino diacetic acid in hydrochloric acid for 72 minutes, an assayed yield of N-phosphonomethyl glycine of 85% was obtained.

In another experiment, the constant current was applied to 18 ml. of the above solution for 80 minutes, and an assayed yield of N-phosphonomethyl glycine of 83% was obtained.

EXAMPLE 6

In this example, graphite anodes and an undivided cell were employed to electrolytically oxidize 9 ml. of 10% N-phosphonomethylimino diacetic acid in 20% aqueous hydrochloric acid containing .5 g. of urea. The temperature was 100° C. and the total time of electrolysis was 22 minutes at 1.2 amps. The reaction mixture was concentrated and assayed. The yield of N-phosphonomethyl glycine was 83% and contained no N-methyl-N-phosphonomethyl glycine by-product.

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EXAMPLE 7

One hundred milliliters of a solution of 5% N-phosphonomethyliminodiacetic acid in 20% hydrochloric acid was recirculated through a reservoir held at 70° C. and an undivided cell. The cell consisted of a tube containing a porous carbon disc anode (8.5 cm.² by 1 inch) and a platinum foil cathode. The solution was pumped through the porous anode at a rate of 100 ml./minute. A current of one ampere was passed through the cell for sixty minutes and 0.5 amps. for 65 minutes. Analysis of the reaction mixture indicated that a yield of 96.6% of N-phosphonomethyl glycine was obtained.

EXAMPLE 8

A bipolar porous electrode cell was employed in the electrolytic oxidation of N-phosphonomethylimino diacetic acid to N-phosphonomethyl glycine. The cell contained three porous graphite electrodes in series with solution flowing through them. The center electrode had no direct electrical connection but operated as a porous bipolar electrode as evidenced by gas evolution from both surfaces when current was passed through the cell via the end electrodes. A solution of 5% N-phosphonomethylimino diacetic acid in 20 hydrochloric acid was passed through the cell while the current was passing. Analysis of the reaction mixture indicated that there was some conversion of N-phosphonomethylimino diacetic acid to N-phosphonomethyl glycine.

EXAMPLE 9

Into an electrolytic cell containing a graphite anode and a graphite cathode was charged N-phosphonomethylimino diacetic acid (10 grams) dissolved in 100 ml. of 20% hydrochloric acid. The cell and contents were heated to approximately 100° C. to cause reflux and the electrolysis then started. A current of 0.5 amps was passed through the solution for 5 hours and the current reduced to 0.25 amperes for an additional 1 1/4 hours. During this time, water, formaldehyde and hydrochloric acid was distilled off continuously, giving a total of 75 ml. of distillate. The cell was kept at approximately constant volume by the addition of 20% hydrochloric acid. After the electrolysis was completed, the reaction mixture was analyzed by nuclear magnetic resonance spectral analysis and found to contain N-phosphonomethyl glycine. The yield in this experiment was 93% of theory.

A similar experiment employing 25 grams of N-phosphonomethylimino diacetic acid dissolved in 100 ml. of 20% hydrochloric acid gave a yield of 80% of N-phosphonomethyl glycine.

EXAMPLE 10

In this example, an electrolytic cell comprising two graphite electrodes having surfaces of 28 centimeters by 5 centimeters and separated by an insulating gasket were employed. The cell was open at the top and was equipped with a pump so that the solution could be pumped through the cell and back to a reservoir which was held at 80-90° C. The cell was also fitted with heating elements. The reservoir was charged with 50 ml. of a 25% solution of N-phosphonomethylimino diacetic acid dissolved in 20% HCl. This solution was pumped through the cell and back to the reservoir. The cell was heated until reflux was observed in the solution. The flow through the cell was maintained at about 40 ml. per minute, and 20% HCl was added to the reservoir to maintain a constant volume. This solution was electrolyzed at 1 ampere for 3 hours. On cooling, analysis of the solution showed that N-phosphonomethyl glycine had been obtained in 85.6% yield.

EXAMPLE 11

In this example, a cell consisting of a tube containing a porous carbon disc anode (approximately 8.5 centimeters squared by 1 inch thick) and a graphite cathode was connected through a pump to a reservoir whereby the reaction mixture could be recirculated through the cell at room temperature. A mixture of N-phosphonomethylimino diacetic acid (11.35 grams), isopropylamine (5.9 grams) and water (100 ml.) was placed in the cell and reservoir. The solution was circulated at room temperature and electrolyzed at about 0.5 amps for 6.5 hours. Analysis of the final solution indicated that the isopropylamine salt of N-phosphonomethyl glycine had been obtained.

EXAMPLE 12

The electrolysis of N-allyl-N-phosphonomethyl glycine (3 g. in 50 ml. of concentrated HCl) was carried out in an apparatus consisting of a cell, reservoir and pump. The electrolysis cell consisted of a glass tube with a 1-inch diameter by 1-inch thick porous graphite anode cemented into the tube. A carbon rod downstream of the anode served as the cathode. The solution was pumped from the reservoir through the cell and back to the reservoir at a rate of 100 ml. per minute during the electrolysis. The electrolysis was carried out at 1 amp for 2 hours at room temperature. After the electrolysis, analysis by proton nuclear magnetic resonance and gas chromatography indicated the presence of N-phosphonomethyl glycine.

EXAMPLE 13

The electrolysis of N-benzyl-N-phosphonomethyl glycine (5 grams in 75 ml. of 20% HCl) was carried out in the apparatus described in Example 12. The electrolysis was carried out at 0.5 amps for 2 hours at room temperature. After the electrolysis, analysis by proton nuclear magnetic resonance and gas chromatography indicated the presence of N-phosphonomethyl glycine.

EXAMPLE 14

The electrolysis of N,N-bis(phosphonomethyl)glycine (5 grams in 50 ml. concentrated HCl) was carried out in the apparatus described in Example 12. The electrolysis was carried out at 1 amp for 2½ hours at room temperature. After the electrolysis, analysis by proton nuclear magnetic resonance indicated the presence of N-phosphonomethyl glycine.

EXAMPLE 15

The electrolysis of N-phosphonomethylimino diacetic acid (5 grams in 100 ml. of 2% HCl) was carried out in the apparatus described in Example 12, except that the solution in the reservoir was maintained at 80° C. with a heater. The electrolysis was carried out at 1 amp for 50 minutes and 0.5 amps for 40 minutes at which time no N-phosphonomethylimino diacetic acid remained in the solution (nuclear magnetic analysis). Analysis of the final solution showed 28.44 mg./ml. of N-phosphonomethyl glycine and 5.79 mg./ml. total phosphorous for a 90.6% yield.

EXAMPLE 16

A 5% (w./w.) solution of N-phosphonomethylimino diacetic acid in 20% hydrochloric acid was passed at a rate of 25 ml./min. through a multi-electrode bipolar cell. The cell consisted of 20 porous graphite blocks, 1" wide x 6" high x 1" thick, with electrical connections only on the end electrodes. Flow was through the 1" thickness. The temperature was 60° C.; applied voltage

was 57 volts and current was 5.0 amperes. The effluent was shown to contain N-phosphonomethyl glycine in 94% yield based on starting material.

EXAMPLE 17

A 10% (w./w.) solution of N-phosphonomethylimino diacetic acid in 20% hydrochloric acid was caused to flow through a multi-electrode monopolar cell at a rate of 8 ml./min. The cell consisted of six porous carbon anodes, 1" wide x 1" thick x 2" high and seven 0.25" diameter graphite rod cathodes mounted between the anodes and at each end. Electrical connection was made to each cathode and each anode. Flow was through the 1" thickness. The temperature was 50-70° C.; current was 21 amperes and voltage was 3.3 volts. The effluent was shown to contain N-phosphonomethyl glycine in 91.6% yield based on starting material.

EXAMPLE 18

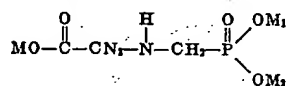
A 5% (w./w.) solution of N-phosphonomethylimino diacetic acid in 20% hydrochloric acid was caused to flow at a velocity of 5 ft./sec. between a solid graphite anode and a solid graphite cathode. The gap between the electrodes was 1/16", the temperature was 70° C., and the electrode dimensions were 39" x 1". The current density was 100 ma./cm.² and 400% of the theoretical current was used. The effluent from the cell contained N-phosphonomethyl glycine in 55% yield.

EXAMPLE 19

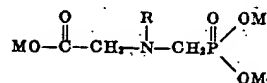
A solution of 150 g. N-phosphonomethylimino diacetic acid and 39 g. isopropylamine in 1.5 liters of water was electrolyzed in an electrolysis cell containing five porous graphite bipolar electrodes at 40 volts and 1.5-2.6 amperes for 2.25 hours. The resulting solution contained the mono-isopropylamine salt of N-phosphonomethyl glycine as shown by its nuclear magnetic resonance spectrum.

What is claimed is:

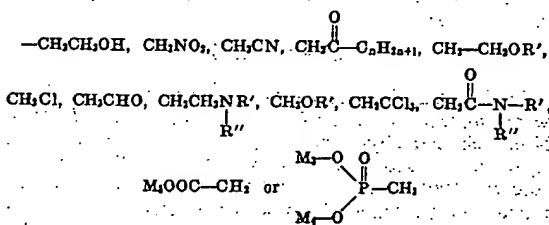
1. A process for producing an N-phosphonomethyl glycine of the formula



wherein M, M₁ and M₂ are each individually hydrogen, alkoxyalkyl groups, alkyl groups of from 1 to 18 carbon atoms, alkali metal, alkaline earth metal, ammonium or organic ammonium provided that at least one of M, M₁ and M₂ is hydrogen, alkali metal or alkaline earth metal which comprises subjecting an aqueous electrolytic medium containing an N-organo-N-phosphonomethylamino acetic acid compound of the formula



wherein R is a member of the class consisting of allyl, halogensubstituted allyl, benzyl, halosubstituted benzyl, 2,2,2-triphenylethyl, diphenylmethyl, 1,2- or 2,2-diphenylethyl,



wherein R' is alkyl of from 1 to 6 carbon atoms, R'' is H or R', n is an integer of 1 to 6, and M₃ and M₄ are as

defined for M , M_1 and M_2 to an electromotive force whereby said acetic acid compound is oxidized to N-phosphonomethyl glycine.

2. A process as claimed in Claim 1 wherein the aqueous electrolytic medium is an acidic aqueous medium.

3. A process as claimed in Claim 2 wherein the acidic aqueous medium is hydrochloric acid.

4. A process as claimed in Claim 3 wherein the hydrochloric acid concentration is from 10 to about 25%.

5. A process as claimed in Claim 1 wherein the process is conducted in an electrolytic cell having noble metal carbon, or graphite electrodes.

6. A process as claimed in Claim 5 wherein both electrodes are carbon or graphite electrodes.

7. A process as claimed in Claim 6 wherein the graphite is porous graphite.

8. A process as claimed in Claim 6 wherein the carbon is porous carbon.

9. A process as claimed in Claim 1 wherein the initial N-organo-N-phosphonomethylamino acetic acid concentration is at least 1% by weight of the total medium.

10. A process as claimed in Claim 1 wherein the aqueous electrolytic medium is a basic aqueous medium.

11. A process as claimed in Claim 1 wherein the concentration of the N - organo-N-phosphonomethylamino acetic acid compound is from about 5% to about 30% by weight of the aqueous electrolytic medium.

12. A process as claimed in Claim 1 wherein the current density is from 1.0 to about 700 ma./cm.².

13. A process as claimed in Claim 1 wherein the aqueous electrolytic medium also contains urea.

14. A process as claimed in Claim 1 wherein the aqueous electrolytic medium contains a salt.

15. The process as claimed in Claim 1 wherein the N-organo-N-phosphonomethylamino acetic acid compound is N-phosphonomethylimino diacetic acid.

16. The process as claimed in Claim 1 wherein the N-organo-N-phosphonomethylamino acetic acid compound is the isopropylammonium salt of N-phosphonomethylimino diacetic acid.

17. The process as claimed in Claim 1 wherein the N-organo-N-phosphonomethylamino acetic acid compound is N-allyl-N-phosphonomethylamino acetic acid.

18. The process as claimed in Claim 1 wherein the N-organo-N-phosphonomethyl acetic acid compound is N-benzyl-N-phosphonomethylamino acetic acid.

19. The process as claimed in Claim 1 wherein the N-organo-N-phosphonomethyl acetic acid compound is bis-(N-phosphonomethyl)amino acetic acid.

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JOHN H. MACK, Primary Examiner

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